

GASIFICATION OF ORGANIC WASTE

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INTRODUCTION

The utilization of solid organic waste has received considerable attention as a result of public concern over a deteriorating environment and an apparent depletion of our natural resources. Up to 70% or 280 million tons of the 400 million tons of municipal and industrial waste created annually can be classified as organic (1, 2). This figure has been predicted to at least double by 1980 (3). However, these figures are small in comparison to the 3/4 billion tons of moisture free organic animal waste produced annually (4). The problems and expense associated with the disposal of these wastes have led investigators to seek new and unique solutions.

Among the oldest and currently most used disposal methods are landfill and incineration. Inherent problems associated with these two methods have been described (5, 6). Methods have been devised and work is continuing on the utilization of the heat created by incineration. Other more innovative utilization processes have been proposed, some of which are currently under investigation. The Bureau of Mines has been investigating two different conversion processes--the pyrolysis method and the hydrogenation process (7,8). The former method produces gas, oil and solids while the latter, which appears to have a greater com-

mercial promise, produces essentially oil. Although these two processes are thought to have general applicability, they have largely employed bovine manure as a feed material. Two other processes, which are somewhat limited in scope, are Firestone's destructive distillation process (9) for converting shredded tires into various useful chemicals and Cities Service--Goodyear process (10) for the production of carbon black from old tires. In this communication the results of a bench-scale feasibility study on the conversion of solid organic waste into a high Btu fuel gas are presented. These results are discussed in reference to the process variables and the experimental equipment employed in the investigation.

EXPERIMENTAL

Reactor Design.--The gasification of the organic waste was carried out in a one inch, batch charge, bench-scale reactor. The schematic is shown in Figure 1 which has been previously described in detail (11). The reactor has been designed so that temperature, pressure and steam input can be controlled over a considerable range.

Feed Materials.--Several types of organic wastes were used as reactor feed materials. These include paper, tire rubber, Denver Municipal Sewage Sludge, animal waste and simulated garbage composed of 4.5% paper, 13.4% polyethylene, 39.5% organic waste, 24.7% tire rubber and 17.9% wood. The chemical analyses of these materials are given in Table I.

Catalysts.--Three different commercially available nickel catalysts were employed. Physical and chemical properties of these catalysts are

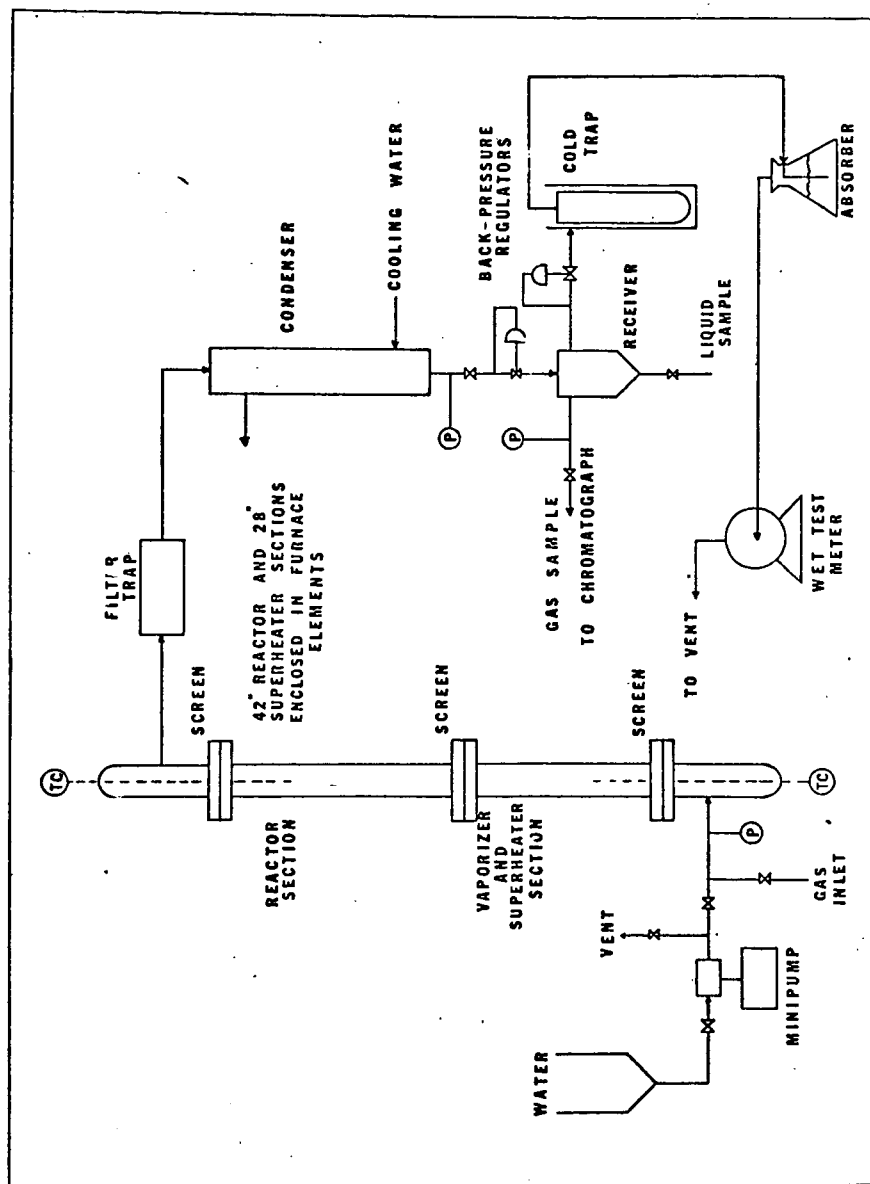


Figure 1. Schematic Flow Diagram.
One Inch Reactor

Table I. Analyses of Feed Materials

	<u>Paper</u>		<u>Sewage Sludge</u>		Scrap Tires	Charred Animal Waste	Raw Garbage ^a Composite
	Raw	Charred	Raw	Charred			
Moisture (wt %)	3.8	0.8	13.6	1.2	0.5		3.4
Hydrogen (wt %)	6.9	3.1	6.7	1.4	4.3	5.4	6.6
Carbon (wt %)	45.8	84.9	28.7	48.6	86.5	41.2	57.3
Nitrogen (wt %)	--	0.1	2.6	3.7	--	1.5	0.5
Oxygen	46.8	--	26.5	--	--	26.0	22.1
Sulfur (wt %)	0.1	0.1	0.6	--	1.2	0.4	0.4
Ash (wt %)	0.4	2.5	34.9	45.7	3.4	25.5	10.2

^a Calculated from composite composition.

listed in Table II. In addition both potassium and sodium carbonates were employed as gasification catalysts.

Analyses.--Except as noted below, the majority of the chemical analyses were carried out by standard laboratory methods. Sulfur analyses were performed on a Leco sulfur analyzer and complimented by standard ASTM methods. Product gas volumes were recorded with a calibrated wet test meter. Product gas compositions were determined with a Beckman Model GC-5 dual column--dual thermal conductivity detector chromatograph equipped with an Auto Lab System IV digital integrator. Calibration values were obtained by use of a Linde primary standard gas mixture.

Methodology.--Experiments were carried out by charging the reactor section with a nickel catalyst and feed material. The feed material was mixed with an alkali carbonate catalyst. Both stratification (integrated) and separation (segregated) of the nickel catalyst and feed material were employed. The reactor was then adjusted to the desired operating conditions and the product gas was sampled for its composition every half hour. The compositions reported in Table III are the average compositions.

RESULTS AND DISCUSSION

It is apparent from the complex composition of the feed materials that the resulting gasification reactions are both varied and complex. Although these reactions may not be known from a mechanistic point of view, experimental observations allow one to formulate a functional description of the overall reactions which incidentally are consistent with those observed in the production of synthetic natural gas from coal.

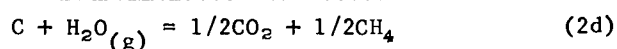
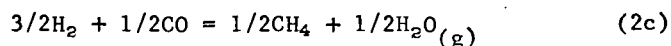
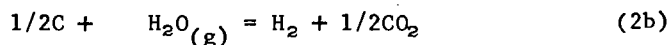
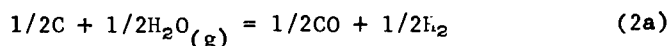
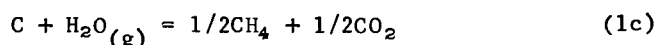
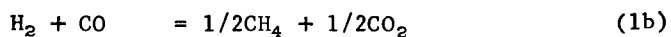
Table II. Catalysts Properties^a

Total Ni (wt %)	Harshaw Ni-0104 58.8	Harshaw Ni-3250 50	Girdler G-65 25
Support Material	Kieselguhr	--	proprietary
Surface Area (m ² /g)	130	150	54
Pore Volume (cc/g)	0.5	0.34	0.08
ABD ^b (lbs/ft ³)	55	68	65
Pellet Shape and Size ^c	1/4 T	1/8 T	3/16 T
Avg. Crush Strength (lbs)	8	18	25

^a Data is for a typical sample.

^b ABD, apparent bulk density.

^c Tablet, T. Sizes are expressed in inches.



It should be noted that the end result in each of these reaction schemes is the same, irregardless of the nature of the intermediate steps. Employing these chemical equations in conjunction with the carbon content of the various organic wastes permits one to calculate a theoretical yield of gas product.

Table III contains a summary of some selected experimental gasification results for the various feed materials and catalysts employed. General observations obtained with the single stage experimental unit indicate that the initial reactions occurring during an experimental run are devolatilization and cracking, particularly in those instances where the volatile material content is high. This is followed by the carbon-steam reaction according to equation 1a which is initiated by the addition of steam. Alkali metal carbonates have been found to catalyze this reaction. Catalytic methanation of the intermediate reactants from the carbon-steam reaction with a nickel catalyst is then effected, apparently by reactions 1b and 2c.

Table III. Organic Waste Conversion Data

Run No.	302	295	489	416	298	297	517
Type							
Feed Material	Integrated Raw Paper	Integrated Charred Paper	Integrated Raw Sewage Sludge	Segregated Charred Sewage Sludge	Integrated Scrap tires	Integrated Charred Animal Waste	Integrated Raw Garbage Composite
Weight (lb)	0.132	0.172	0.275	0.275	0.207	0.220	0.240
Catalyst	Ni-0104	Ni-0104	Ni-3250	Ni-3250	Ni-0104	Ni-0104	G-65
Weight (lb)	0.165	0.191	0.220	0.275	0.220	0.220	0.275
K ₂ CO ₃ (lb)	0.0330	0.0441	0.0331	0.0660	0.0551	0.0551	0.0440
Pressure (psia)	261	261	32	261	266	266	32
Ave. Temperature (°C)	710	740	670	390 ^b	700	670	660
Gas Composition (mole %)							
CO	0.0	0.0	0.0	0.0	0.0	0.0	0.1
CO ₂	48.0	42.7	44.8	48.9	49.3	48.2	42.0
H ₂	8.8	10.4	3.2	6.7	1.5	5.0	4.2
C ₁	43.2	47.5	52.0	44.5	49.3	46.9	53.7
unsats	0.0	0.0	0.0	0.0	0.0	0.0	0.0
>C ₁	0.0	0.0	0.0	0.0	0.0	0.0	0.0
SCF CH ₄ /Ton	9,533	13,169	6,335	5,508	23,333	12,881	7,489
Theoretical CH ₄ (SCF/Ton) ^a	12,823	25,410	6,917	6,822	27,320	13,012	17,150
CH ₄ Yield (%)	74	52	92	81	85	99	44
Btu/SCF (CO ₂ -free)	884	883	973	923	981	937	963

^aBased on equation 2d and carbon content of feed material.^bApparent gasification temperature was ~720°C. Apparent catalyst temperature was ~390°C.

The purpose of the addition of alkali carbonate to the feed material is to catalytically promote the carbon-steam reaction. This effects rates that would otherwise be prohibitively slow at these lower temperatures (650 - 750°C) in the absence of the catalyst. Potassium carbonate, sodium carbonate and sodium sesquicarbonate have been employed with no apparent chemical preference under experimental conditions. However, from an economic point of view the sodium sesquicarbonate is the cheaper material. Although optimum alkali metal carbonate/carbon weight ratios have not been well defined, values between 12-25% have been found to give satisfactory results. These observations concerning the alkali carbonate catalysts are analogous to those found for the production of water gas from coal-steam reactions (12, 13).

The conversion of the intermediate reactants produced in the carbon-steam reaction are catalytically converted to methane, carbon dioxide and water by a methanation catalyst. Of the three catalysts employed, which have significantly different chemical compositions and physical properties, no apparent difference in their methanating ability under experimental conditions were observed. However, the catalyst's ability to produce significant quantities of methane from the initially produced gaseous reactants depends upon maintaining the nickel catalyst in a highly reduced state and protected from the air. This is achieved by reducing in situ and employing inert atmosphere techniques. In addition, the steam fed to the reactor must be judiciously controlled in order to preserve the methanation catalyst's activity, yet provide enough steam to maintain a reasonable carbon-steam reaction rate. Excessive amounts

of steam will cause the gas composition to shift from low H_2 , high CO_2 and CH_4 to high H_2 , CO_2 and moderate amounts of CO . This shift is apparently due to reaction 2b as a result of the increase in the partial pressure of steam and possible catalyst oxidation. This CO -shift is accompanied by a drastic reduction in the volume heating value of the product gas.

The overall gasification process was found to be independent of pressure under experimental conditions. Thus, even though pressures of 261 psia were employed the results were essentially the same as obtained at 32 psia. This observation is consistent with theoretical predictions based upon equation 1c for an integrated reactor.

The temperature of the gasification process is a compromise between that necessary for the carbon-steam reaction and that for optimum methanation. This compromise is necessary when working with a one-stage process as opposed to a two-stage process. In the latter instance the temperature of each stage (carbon-steam and methanation reactions) can be adjusted for optimization. Depending upon concentrations of the gaseous reactants, the optimum temperature lies in the 590 - 675°C range for a single-stage process which is consistent with some thermodynamic calculations for the system (14).

Irrespective of the organic waste material employed, the gasification results were generally above 75% of the theoretical methane value. The quantity of gaseous product was proportional to the carbon content when other factors were held constant. Hence, as demonstrated by Table III, rubber tires which contain about 85 wt % carbon produced 23,000 SCF

CH₄/ton while Denver metropolitan sewage sludge with 26 wt % carbon yielded only 6300 SCF CH₄/ton. The sewage sludge was unusual from the standpoint that liquid hydrocarbons were also produced from its gasification. This liquid hydrocarbon production is believed to be attributed to the iron content (6 wt %) in the sludge which is introduced during municipal treatment. Iron has long been known to function as a Fisher-Tropsch catalyst.

Table IV contains a tabulation of volume contraction of the organic waste upon gasification. These values are based on apparent bulk densities for each of the feed materials. Also included within the table is a comparison between the theoretical potential energy value of the feed material that would be realized through combustion and that obtained through its conversion to a synthetic natural gas. The potential energy value of the synthetic natural gas is observed to be considerably less than that for combustion. This is largely a consequence of the chemical reactions involved in the two different processes. Furthermore, it must be realized that the efficiency of the conversion of the heat energy, created by incineration, into a usable and transportable energy form will decrease the difference between the two. Fernandes and Cohan (15) have computed the energy available from the incineration of mixed refuse containing 27% carbon and 4.5% hydrogen to be 3150 Btu/lb.

CONCLUSIONS

Exploratory experiments have shown that organic waste materials can be converted to gaseous fuel products composed essentially of CH₄, CO₂ and H₂ with a CO₂-free heating value in excess of 900 Btu/SCF. Furthermore, the overall conversion has been shown to be pressure

Table IV. Volume Contractions and Potential Energy Comparisons

Gasified Material	Run No.	% Volume Contraction	Calculated		% Potential Energy Recovered
			Heating Value of Reactant Material (Btu/lb reactant)	Experimental Heating Value (CO ₂ -free) of Gas Product (Btu/lb reactant)	
Raw Paper	320	93.9	10020	5120	51
Charred Paper	295	62.2	13560	7090	52
Raw Sewage Sludge	489	61.9	7500	3270	44
Charred Sewage Sludge	416	43.1	7570	2920	39
Scrap Tires	298	83.3	14410	11780	82
Charred Animal Waste	297	63.4	8590	6680	78
Raw Garbage Composite	517	66.4	11480	3890	34

independent over the range of 32-261 psia while the optimum temperature (650 - 750°C) for the described process is strongly dependent upon the composition of the primary gaseous reactants produced from the steam-carbon reaction which is catalyzed by the presence of alkali carbonates.

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